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Preliminary communication

METAL COMPLEXES AS DONOR LIGANDS: FORMATION OF METAL—METAL BONDED SPECIES VIA INTRAMOLECULAR REARRANGEMENT

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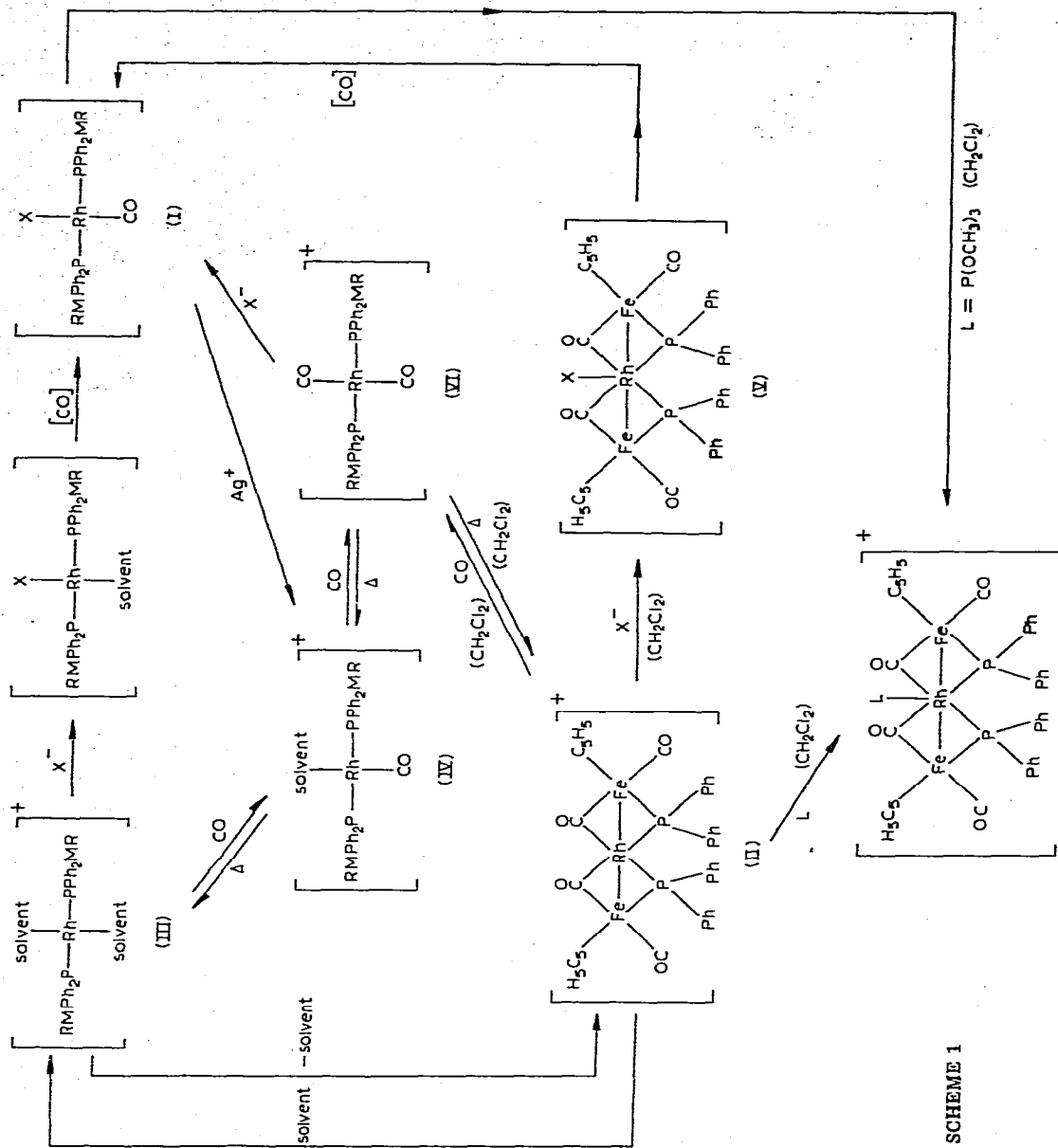
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Summary

The reactions of the metal-containing phosphines and sulphides, $P(C_6H_5)_2MR$ and $SR'MR$ [$MR = Fe(CO)_2(\eta^5-C_5H_5)$; $R' = C_2H_5$, $t-C_4H_9$ or C_6H_5] with various rhodium(I) derivatives, are described; $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta^5-C_5H_5)\}_2]^+$, which contains bridging as well as terminal carbonyls, reacts reversibly with carbon monoxide and weakly coordinating solvents to afford species containing terminal carbonyls only.

It is well established that reaction of $[Rh(CO)_2Cl]_2$ with excess $P(C_6H_5)_3$ in benzene or ethanol gives neutral $[Rh(CO)\{P(C_6H_5)_3\}_2Cl]$ in high yield [1-4]. We have found that treatment of this rhodium carbonyl dimer with the metal-containing tertiary phosphine $P(C_6H_5)_2MR$ [$MR = Fe(CO)_2(\eta^5-C_5H_5)$] in benzene leads to the formation of a similar neutral product viz. $[Rh(CO)\{P(C_6H_5)_2MR\}_2Cl]$ (I). In contrast, as reported previously [5], this reaction when performed in methanol in the presence of a large counterion such as SbF_6^- affords the novel ionic metal—metal bonded compound, $[Rh\{FeP(C_6H_5)_2(CO)_2(\eta^5-C_5H_5)\}_2]SbF_6$, shown by means of an X-ray diffraction study to have structure II in the crystalline state [5, 6]. This structure is retained by the compound in non-coordinating solvents, as established by means of infrared spectroscopy [$\nu(C-O)$ 2013s, 1852m and 1823m cm^{-1} , measured in CH_2Cl_2 ; $\nu(C-O)$ 2008s, 1851m and 1826m cm^{-1} , measured as Nujol mull], but in coordinating solvents such as acetone, tetrahydrofuran, diglyme, methanol, nitromethane, acetonitrile or pyridine the infrared data are consistent with solvent coordination leading to derivatives containing terminal carbonyls only and presumed to be the solvento

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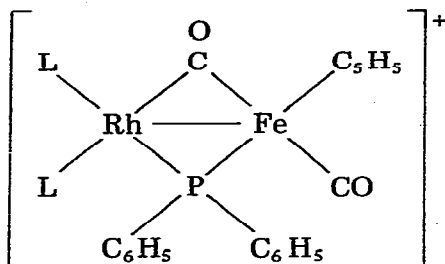
species III [$\nu(\text{C—O})$ 2026s, 1976s and 1960 cm^{-1} (ip)*, measured in acetone; $\nu(\text{C—O})$ 2032s and 1992s cm^{-1} , measured in acetonitrile]. Significantly, this solvent interaction is reversible and evaporation of solutions of the solvento species leads to recovery of the parent compound II.

Compounds I and II are readily interconvertible. Thus treatment of $[\text{Rh}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_2\text{MR}\}_2\text{Cl}]$ with AgSbF_6 in acetone, alcohol or tetrahydrofuran affords a solution, undoubtedly containing $[\text{Rh}(\text{CO})\{\text{P}(\text{C}_6\text{H}_5)_2\text{MR}\}_2(\text{solvent})]^+$ (IV) on the basis of previous findings [7], from which $[\text{Rh}\{\text{FeP}(\text{C}_6\text{H}_5)_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}_2]^+$ (II) can be isolated. The neutral halide I is regenerated when II is treated with chloride ions. This chloride ion attack as well as that by other halide and pseudohalide ions produces initially in non-coordinating solvents the metal-metal bonded species V as intermediate but this readily absorbs carbon monoxide to give I. The formation of I is considerably accelerated by passage of carbon monoxide through the solution.

Reaction of $[\text{Rh}\{\text{FeP}(\text{C}_6\text{H}_5)_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}_2]^+$ (II) with carbon monoxide gives $[\text{Rh}(\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_2\text{MR}\}_2]^+$ (VI), suggested to have a *trans* configuration analogous to $[\text{Rh}(\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}_2]^+$ [8]. This reaction is reversible and heating of a solution of VI regenerates the bridging carbonyl species II. Significantly, reaction of $[\text{Rh}(\text{CO})_2\{\text{P}(\text{C}_6\text{H}_5)_2\text{MR}\}_2]^+$ (VI) with halide ions gives I as outlined in Scheme 1.

Sulphido derivatives analogous to $[\text{Rh}\{\text{FeP}(\text{C}_6\text{H}_5)_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}_2]^+$ (II) are obtained by reaction of $\text{SR}'\text{MR}$ [$\text{R}' = \text{C}_2\text{H}_5$ or $t\text{-C}_4\text{H}_9$; $\text{MR} = \text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$] with $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{ethanol})_x]^+$ in ethanol. However treatment of $[\text{Rh}(\text{C}_8\text{H}_{12})(\text{ethanol})_x]^+$ with $\text{S}(\text{C}_6\text{H}_5)\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ in this solvent gave $[\text{Rh}(\text{C}_8\text{H}_{12})\{\text{S}(\text{C}_6\text{H}_5)\text{MR}\}_2]^+$ containing terminal carbonyl groups only. All attempts to convert the latter into $[\text{Rh}\{\text{FeS}(\text{C}_6\text{H}_5)(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)\}_2]^+$ (II) were unsuccessful. Also treatment of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ with $\text{S}(\text{C}_6\text{H}_5)\text{MR}$ in benzene gave $[\text{Rh}(\text{CO})_2\text{SC}_6\text{H}_5]_2$ [9], not $[\text{Rh}(\text{CO})\{\text{S}(\text{C}_6\text{H}_5)\text{MR}\}_2\text{Cl}]$.

The rearrangement of derivatives containing $\text{P}(\text{C}_6\text{H}_5)_2\text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ to form metal-metal bonded species is not restricted to those in which two of these tertiary phosphine ligands are present. Thus treatment of $[\text{L}_2\text{Rh}(\text{solvent})_x]\text{SbF}_6$ [$\text{L} = \text{P}(\text{OC}_6\text{H}_5)_3$; $\text{L}_2 = \text{C}_8\text{H}_{12}$] with an equimolar amount of $\text{P}(\text{C}_6\text{H}_5)_2\text{MR}$ [$\text{MR} = \text{Fe}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$] gives products characterised as $[\text{L}_2\text{RhFeP}(\text{C}_6\text{H}_5)_2(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)]\text{SbF}_6$. The infrared data for these compounds are consistent with structure VII [$\text{L} = \text{P}(\text{OC}_6\text{H}_5)_3$: $\nu(\text{C—O})$ 2028s and 1850m cm^{-1} , measured in CH_2Cl_2 ; $\text{L}_2 = \text{C}_8\text{H}_{12}$: $\nu(\text{C—O})$ 2013s and 1834m cm^{-1} , measured in CH_2Cl_2].



(VII)

*ip = inflexion point.

It is apparent that reaction of metal-containing ligands of the type employed with transition metal derivatives provides a direct method for the synthesis of metal-metal bonded and possibly of cluster species, provided that the initial complex formed is coordinatively unsaturated or contains weakly bound ligands and that intramolecular rearrangement can readily occur.

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